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Author: Qili Hu Nan Chen Chuanping Feng WeiWu Hu

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Highlights:

- Granular chitosan-Fe$^{3+}$ complex had high performance for nitrate adsorption
- Granular chitosan-Fe$^{3+}$ complex had shorter equilibrium time (1.5 h)
- Nitrate adsorption was ascribed to ion exchange and electrostatic attraction
- Granular chitosan-Fe$^{3+}$ complex could be regenerated using NaCl solution
Nitrate adsorption from aqueous solution using granular chitosan-Fe$^{3+}$ complex

Qili Hu$^{a,b}$, Nan Chen$^{a,b,*}$, Chuanping Feng$^{a,b}$, WeiWu Hu$^{c}$

$^a$ School of Water Resources and Environment, China University of Geosciences (Beijing), Beijing, 100083, China

$^b$ Key Laboratory of Groundwater Cycle and Environment Evolution (China University of Geosciences (Beijing)), Ministry of Education, Beijing, 100083, China

$^c$ The Journal Center, China University of Geosciences (Beijing), Beijing, 100083, China

* Corresponding author: Nan Chen, School of Water Resources and Environment, China University of Geosciences (Beijing), Beijing, 100083, China.
Tel: +86 10 82322281
Fax: +86 10 82321081
E-mail: chennan@cugb.edu.cn (N. Chen)
Abstract

In the present study, In order to efficiently remove nitrate, granular chitosan-Fe$^{3+}$ complex with high chemical stability and good environmental adaptation was synthesized through precipitation method and characterized using SEM, XRD, BET and FTIR. The nitrate adsorption performance was evaluated by batch experiments. The results indicated that granular chitosan-Fe$^{3+}$ complex was an amorphous and mesoporous material. The BET specific surface area and average pore size were 8.98 m$^2$ g$^{-1}$ and 56.94 Å, respectively. The point of zero charge was obtained at pH 5. The maximum adsorption capacity reached 8.35 mg NO$_3^-$-N g$^{-1}$ based on Langmuir-Freundlich model. Moreover, no significant change in the nitrate removal efficiency was observed in the pH range of 3.0-10.0. The adverse influence of sulphate on nitrate removal was the most significant, followed by bicarbonate and fluoride, whereas chloride had slightly adverse effect. Adsorption process followed the pseudo-second-order kinetic model, and the experimental equilibrium data were fitted well with the Langmuir-Freundlich and D-R isotherm models. Thermodynamic parameters revealed that nitrate adsorption was a spontaneous and exothermic process. Granular chitosan-Fe$^{3+}$ complex could be effectively regenerated by NaCl solution.

Keywords: Nitrate, Granular chitosan-Fe$^{3+}$ complex, Adsorption, isotherm, Regeneration
1 Introduction

The current problem of excess nitrate has gained significant attention in surface and ground water around the world. The extensive use of nitrogen fertilizers and improper treatment of wastewater from industrial sites were presumably responsible for nitrate contamination [1]. High concentration of nitrate in drinking water would pose a serious threat to human health such as liver damage, cancers and methemoglobinemia [2]. Therefore, it was essential to lower the nitrate concentration within a maximum contaminant level (MCL) of 50 mg L$^{-1}$ (as NO$_3^-$) in drinking water [3]. Elevated nitrate concentration surpassing self-purification capacity of water body had a negative impact on ecosystem sustainability including eutrophication caused by heavy algal growth [4].

Nitrate could chronically exist in surface and ground water due to its high solubility and poor adsorption property, which increased difficulty of nitrate removal [5]. Various methods had been developed for the nitrate removal from water and wastewater to reduce the risks to environment, including biological denitrification [6], ion exchange [7], electrochemical reduction [8], reverse osmosis [9], catalytic reduction [10] and adsorption [11]. However, biological method was in need of addition of carbon source and disposal of large amounts of biomass waste [12]. Ion exchange required disposal of waste brine and renewal of costly ion exchange resin. The electrodes were easily inactive in electrochemical reduction. Reverse osmosis had high operational cost. Catalytic reduction could produce the hazardous by-products such as nitrite and ammonia.

Adsorption was found to be superior to other techniques in terms of its low cost, ease of operation and simplicity of design [13]. Recently, many adsorbents such as carbon-based adsorbent [14], mineral-based adsorbent [15] and agricultural waste [16]...
were employed to remove nitrate from aqueous solution. However, these materials had some inherent limitation including small particle size or low desorption efficiency, which might hinder their practical application. Some modified techniques such as surface protonation [11], metal ions immersion [17] and surfactant modified mineral [18] were also applied to enhance their adsorption of nitrate. Nevertheless, some modifiers for adsorbent synthesis had a potential adverse effect on environment. As a consequence, developing an easily reusable, technically feasible and environmentally friendly adsorbent was of prime importance for the nitrate removal.

Chitosan, a natural product derived from deacetylation of the polysaccharide chitin, had received vast interests due to its excellent properties, such as abundant source, non-toxicity, biodegradability and adsorption properties [19]. Chitosan containing enormous free amino and hydroxyl groups had the ability to coordinate with many transition metal ions through a chelation mechanism [20]. Granular chitosan-Fe$^{3+}$ complexes prepared by different approaches had successfully employed to adsorb textile dye [21], Cr(VI) [22], phosphate [23] and As(III) [24]. However, there were few reports for using granular chitosan-Fe$^{3+}$ complex as an adsorbent to remove nitrate from aqueous solution.

To verify the feasibility of granular chitosan-Fe$^{3+}$ complex for the nitrate removal, nitrate adsorption performance was evaluated by investigating the effect of adsorbent dosage, initial NO$_3^-$-N concentration, contact time, pH and co-existing ions on the nitrate removal in this study. Adsorption isotherm and adsorption kinetics were studied to reveal the nitrate adsorption mechanism of granular chitosan-Fe$^{3+}$ complex. Furthermore, desorption studies were also conducted to evaluate the reusability of adsorbent.

2 Materials and methods
2.1 Materials

Chitosan (deacetylation degree = 80.0%–95.0%) was purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Ferric chloride was obtained from Tianjin Fuchen Chemical Regeats factory, Tianjin, China. Ammonia solution was provided by Beijing Chemical Works, Beijing, China. A series of various concentrations of nitrate solution required were prepared by dissolving NaNO$_3$ in deionized water. All chemicals used in this study were of analytical grade without further purification.

2.2 Adsorbent synthesis

Chitosan powder (9.0 g) was dispersedly dissolved in 0.2 M FeCl$_3$ aqueous solution (300 mL), and then stirred at room temperature for 1.5 h. Subsequently, the resulting chitosan-Fe$^{3+}$ solution was drop wise added into ammonia solution (12.5% v/v) using a disposable syringe. After stabilized for 1.0 h, the spherical hydrogel beads formed were separated and sufficiently washed with deionized water, then dried at 50°C for 7.5 h. The dried beads were immersed in deionized water (liquid-solid ratio of 10 mL g$^{-1}$) at 40°C for 4 h in a horizontal shaker (HZC-280, Bing, China). The swelling effect occurred during the immersion, which would contribute to improving adsorbent surface property and promoting adsorption capacity. After separation, washing and drying, granular chitosan-Fe$^{3+}$ complexes were obtained, and then stored in sealed plastic bag at room temperature for further study. Additionally, the chitosan beads were prepared to compare the nitrate adsorption capacity with granular chitosan-Fe$^{3+}$ complex. In the present study, granular chitosan-Fe$^{3+}$ complex with a particle size range of 1.04-1.16 mm was a spherical and epigranular adsorbent, which was superior to hydrotalcite [25] and modified beet residue [26] whose particle sizes were less than 150 $\mu$m and 4.1 $\mu$m, respectively.
2.3 Batch experiments

100 mL of nitrate solution was poured in 250 mL conical flasks for batch experiments, which were sealed and agitated at 140 rpm in a thermostatic shaker (HZC-280, Bing, China) at 25°C for 1.5 h.

2.3.1 Evaluation of adsorption performance

The experiments for evaluation were performed at initial nitrate concentration of 50 mg NO$_3$-N L$^{-1}$ and 20 g L$^{-1}$ of adsorbent dosage.

The effect of adsorbent dosage was investigated at the addition of 5, 10, 15, 25, 30 and 40 g L$^{-1}$. The initial pH of nitrate solution was adjusted in the pH range from 3.0 to 12.0 using 0.1 M HCl or 0.1 M NaOH solution. In order to investigate the effect of co-existing ions, anions (Cl$^-$, HCO$_3^-$, F$^-$ and SO$_4^{2-}$) were added at every anion concentration of 4 mmol L$^{-1}$, and cations (K$^+$, Na$^+$, NH$_4^+$, Ca$^{2+}$, Mg$^{2+}$) were added by fixing a chloride ion concentration at 4 mmol L$^{-1}$.

2.3.2 Kinetic, isotherm and thermodynamic studies

These studies were performed at adsorbent dosage of 20 g L$^{-1}$.

Kinetic studies were carried out at different nitrate concentrations (20, 50 and 100 mg NO$_3$-N L$^{-1}$) at certain intervals (5, 10, 15, 20, 25, 35, 45, 60, 90 and 120 min).

Isotherm studies were performed at different initial concentrations (20, 30, 40, 50, 75, 100, 120, 150, 180 and 200 mg NO$_3$-N L$^{-1}$). Thermodynamic studies were conducted at 15, 25, 35, 45 and 55°C.

Adsorption capacity of granular chitosan-Fe$^{3+}$ complex was calculated at equilibrium using the following equation [13]:

$$ q_e = \frac{(C_0 - C_e) \times V}{M} \quad (1) $$

where $q_e$ (mg g$^{-1}$) is the amount of nitrate adsorbed at equilibrium, $C_0$ (mg L$^{-1}$) and $C_e$ (mg L$^{-1}$) are the initial and equilibrium NO$_3$-N concentration in aqueous solution,
respectively. \( V \) (L) is volume of nitrate solution and \( M \) (g) is the mass of adsorbent used.

2.4 Analysis

The concentration of NO\(_3\)-N was determined by standard colorimetric method using a UV/vis spectrophotometer (DR 6000, HACH, USA). The surface morphology and particle size were observed with a scanning electron Microscope (SEM) (SSX–550, Shimadzu, Japan). The crystal structure of granular chitosan-Fe\(^{3+}\) complex was carried out by quantitative X-ray diffraction (XRD) (D8 Focus, Bruker, Germany). The point of zero charge of granular chitosan-Fe\(^{3+}\) complex was estimated by batch equilibrium techniques described by Chutia et al. [27]. The specific surface area and BJH (Barrett-Joyner-Halenda) pore size distribution of granular chitosan-Fe\(^{3+}\) complex were determined using Brunauer-Emmett-Teller (BET) specific surface analysis device (JW-BK132F, JWGB, China). FTIR spectra of chitosan beads and granular chitosan-Fe\(^{3+}\) complex before and after nitrate adsorption were recorded on a Fourier transform infrared spectrometer using KBr pellets over the wavenumber range of 4000-400 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\) (Nexus 470, Thermo Nicolet, USA).

3 Results and discussion

3.1 Characterization of granular chitosan-Fe\(^{3+}\) complex

3.1.1 SEM

SEM images of granular chitosan-Fe\(^{3+}\) complex before and after nitrate adsorption were shown in Fig. 1a and Fig. 2b. It was evident that granular chitosan-Fe\(^{3+}\) complex possessed poorly developed pore and extremely heterogeneous surface morphology, which were partially attributed to the uneven volatilization of ammonia and water molecule on the chitosan-Fe\(^{3+}\) hydrogel beads surface during desiccation. The irregular surface with fingerprint-like textures increased specific surface area and
thereby provided more active sites for nitrate adsorption. Adsorbent surface before nitrate adsorption was observed at a compact gel state, while adsorbent surface after nitrate adsorption had higher surface roughness. This phenomenon was due to the occurrence of swelling effect of granular chitosan-Fe$^{3+}$ complex in the process of nitrate adsorption.

**Fig. 1.** SEM images before nitrate adsorption (a) and after nitrate adsorption (b); XRD pattern (c); Adsorption BJH (Barrett–Joyner–Halenda) pore size distribution (d).

### 3.1.2 XRD

The XRD pattern of granular chitosan-Fe$^{3+}$ complex was illustrated in Fig. 1c. The crystalline peak of this adsorbent was not observed, suggesting that granular chitosan-Fe$^{3+}$ complex exhibited amorphous nature. This behavior was in agreement with other study where Ti-Al binary metal oxide supported chitosan beads was prepared by Thakre et al. [28].

### 3.1.3 Specific surface area

The BET specific surface area, total pore volume and average pore size of granular chitosan-Fe$^{3+}$ complex were found to be 8.98 m$^2$ g$^{-1}$, 0.019 cm$^3$ g$^{-1}$ and 56.94 Å respectively. Granular chitosan-Fe$^{3+}$ complex with the small specific surface area had high adsorption capacity, indicating this adsorbent had a good affinity for nitrate. As was shown in Fig. 1d, the observed pore sizes mostly varied between 2 and 50 nm, accounting for 89.6%. According to the IUPAC classification, the BJH adsorption pore size distribution revealed the mesoporous nature of granular chitosan-Fe$^{3+}$ complex. Furthermore, this pore size range was conductive to the penetration of nitrate into the inner layer of the adsorbent due to very small ionic radius of nitrate.
3.1.4 FTIR

The FTIR spectra were analyzed to identify the vital functional groups accounting for the nature of nitrate adsorption. The broad and intense adsorption band at approximately 3419 cm\(^{-1}\) for the spectrum of pristine chitosan (curve a in Fig. 2) was ascribed to intermolecular hydrogen bonds and the overlap between O–H and N–H stretching vibration. The characteristic peaks at 2923 and 2881 cm\(^{-1}\) were assigned to C–H stretching vibration of –CH\(_2\) and –CH\(_3\) aliphatic groups, respectively [29]. Two new peaks appeared at 2337 and 2363 cm\(^{-1}\) were attributed to the amino protonation of –NH\(_2\) and –NHCOCH\(_3\) group. The peak at 1648 and 1559 cm\(^{-1}\) referred to C=O stretching vibration of acetyl group and the stretching vibration of amine group, respectively. The peaks at 1155, 1032, 1419 and 1384 cm\(^{-1}\) were related to C–O–C stretching vibration and C–H symmetric bending vibration, separately. It had been reported that the characteristic peak of NO\(_3^-\) existed at around 1384 cm\(^{-1}\) [30]. The peak at 1261 and 1073 cm\(^{-1}\) corresponded to the stretching vibration of C–O in chitosan molecule on C-3 and C-6 position, respectively. It was observed that C–H out-of-plane bending vibration and N–H wagging vibration occurred at ca. 898 and 660 cm\(^{-1}\) [31].

It was clearly seen from the curve b in Fig. 2 that the peaks at 1559 and 660 cm\(^{-1}\) disappeared for chitosan after reaction, and the transmittances at 2374 and 2341 cm\(^{-1}\) sharply increased due to the occurrence of dipole moment change compared with original chitosan, which implied that the interaction did occur between nitrate ions and protonated amine groups. Moreover, it was observed from the curve c and d in Fig. 2 that there were few changes as to the FTIR spectra of granular chitosan-Fe\(^{3+}\) complex before and after nitrate adsorption, indicating no new chemical bond appeared between nitrate ions and granular chitosan-Fe\(^{3+}\) complex.
Fig. 2. FTIR spectra: chitosan before nitrate adsorption (a); chitosan after nitrate adsorption (b); chitosan-Fe$^{3+}$ complex before nitrate adsorption (c); chitosan-Fe$^{3+}$ complex after nitrate adsorption (d).

3.2 Effect of adsorbent dosage

Adsorbent dosage was a vital parameter influencing adsorption capacity and effluent concentration [32]. The effect of adsorbent dosage on nitrate removal was depicted in Fig. 3. It was evident that the nitrate removal efficiency increased from 27.6% to 90.4% with the increase in adsorbent dosage from 2 to 40 g L$^{-1}$. The increment was ascribed to availability of more active sites and larger surface area at higher dosage [33]. However, the equilibrium adsorption capacity of adsorbent decreased from 6.99 to 1.15 mg NO$_3^-$-N g$^{-1}$, which was due to the fact that the increase in adsorbent dosage for a given amount of nitrate resulted in unsaturation of adsorption sites [34]. Moreover, it was found that further increase in dosage beyond 20 g L$^{-1}$ rarely affected adsorption capacity of adsorbent. Adsorption capacity of granular chitosan-Fe$^{3+}$ complex reached 2.04 mg NO$_3^-$-N g$^{-1}$ compared with granular chitosan-Fe$^{3+}$ complex (1.38 mg NO$_3^-$-N g$^{-1}$) that was not immersed in deionized water.

Fig. 3. Nitrate removal efficiency and adsorption capacity under different dosage conditions (initial concentration = 50 mg NO$_3^-$-N L$^{-1}$, contact time = 1.5 h, temperature = 25°C, pH = 5.9 ± 0.2).

3.3 Effect of pH
The pH of solution affected not only surface charges and dissociation of functional
groups, but also chemical speciation and diffusion rate of solute [35,36]. In the
present study, the point of zero charge was obtained at pH 5.4. The influence of initial
pH on nitrate removal was illustrated in Fig. 4. It was observed that no significant
change occurred in terms of nitrate removal efficiency exceeding 80% in the pH range
of 3.0-10.0, indicating adsorption process was almost independent of initial pH.
Moreover, adsorption capacity of granular chitosan-Fe\textsuperscript{3+} complex (2.04 mg NO\textsubscript{3}\textsuperscript{-N g\textsuperscript{-1}}) was superior to chitosan (1.95 mg NO\textsubscript{3}\textsuperscript{-N g\textsuperscript{-1}}) at an initial concentration of 50 mg NO\textsubscript{3}\textsuperscript{-N L\textsuperscript{-1}} and adsorption dosage of 20 g L\textsuperscript{-1}, implying electrostatic attraction
between negatively charged nitrate ions and positively charged anime groups of
chitosan was not a unique mechanism of nitrate removal [37]. However, the free
amine groups of chitosan could not be protonated at alkaline medium, which did not
facilitate electrostatic attraction. Anion was proposed to be adsorbed on adsorbent
through nonspecific adsorption including electrostatic attraction or specific adsorption
involving ion exchange [38]. Besides, when the pH of solution was higher than the
point of zero charge, negatively charged adsorbent surface will fail to adsorb nitrate
ions due to electrostatic repulsion. For these reasons, ion exchange mainly occurred
between exchangeable chloride ions of adsorbent and nitrate ions in alkaline solution,
which was consistent with the results of D-R isotherm model. These results could be
elucidated by the following reactions.

\begin{align*}
R - NH_2 + H^+ + NO_3^- & \rightarrow R - NH_3^+ \cdots NO_3^- & (2) \\
\equiv Fe - OH + H^+ + NO_3^- & \rightarrow Fe - OH_2^+ \cdots NO_3^- & (3) \\
R - NH_3Cl + NO_3^- & \rightarrow R - NH_2NO_3^+ + Cl^- & (4) \\
\equiv Fe - Cl^- + NO_3^- & \rightarrow Fe - NO_3^- + Cl^- & (5)
\end{align*}
The sharp decrease in nitrate removal efficiency appeared when initial pH exceeded 11.0, which was probably ascribed to the competition between hydroxide and nitrate ions for adsorption sites and the increase in diffusion resistance of nitrate caused by abundant hydroxide ions [28]. In addition, the final pH of solution was located between 5.0 and 6.0, indicating granular chitosan-Fe\textsuperscript{3+} complex had buffer capacity in the pH range of 3.0-10.0.

**Fig. 4.** Effect of pH on nitrate removal efficiency (adsorbent dosage = 20 g L\textsuperscript{-1}, initial concentration = 50 mg NO\textsubscript{3}\textsuperscript{-}N L\textsuperscript{-1}, contact time = 1.5 h, temperature = 25°C, pH = 5.9 ± 0.2).

### 3.4 Effect of co-existing ions

The nitrate-contaminated water generally contained a series of chemical compositions, which could exert a negative influence on adsorption process. Consequently, it was extremely important to explore the effect of co-existing ions on nitrate removal in binary component solution. As was shown in Fig. 5, anions presenting in nitrate solution had a detrimental effect on adsorption process, resulting in the decrease in nitrate removal efficiency. The adverse influence of sulphate on nitrate removal was the most significant, followed by bicarbonate and fluoride, whereas chloride had slightly adverse effect. These anions occupied adsorption sites on the adsorbent surface and increased electrostatic repulsion between granular chitosan-Fe\textsuperscript{3+} complex and nitrate ions, leading to the decrease in nitrate removal efficiency. Wan et al. [25] pointed out that multivalent anion with higher charge density was adsorbed more readily than monovalent anion. Thus, granular chitosan-Fe\textsuperscript{3+} complex had a greater affinity for sulphate ions compared with other anions.
On the other hand, the nitrate removal efficiency had no distinct difference among five cations, implying these cations did not disturb nitrate adsorption. The decrease in nitrate removal efficiency was caused by the competition between nitrate and chloride ions for adsorption sites.

**Fig. 5.** Effect of co-existing ions on nitrate adsorption (adsorbent dosage = 20 g L$^{-1}$, initial concentration = 50 mg NO$_3^-$-N L$^{-1}$, contact time = 1.5 h, temperature = 25°C, pH = 5.9 ± 0.2).

3.5 Effect of initial nitrate concentration and adsorption isotherm

In the present study, adsorption capacity increased dramatically from 0.90 to 4.62 mg NO$_3^-$-N g$^{-1}$ with the increase in initial NO$_3^-$-N concentration, because higher concentration gradient acting as a driving force overcame mass transfer resistance between bulk solution and adsorbent surface [39]. Few sufficient adsorption sites accommodated nitrate ions for a certain amount of adsorbent when nitrate content exceeded a certain concentration, resulting in the decrease in removal efficiency from 93.1% to 47.1% with the increase in initial concentration from 20 to 200 mg NO$_3^-$-N L$^{-1}$.

Adsorption isotherm models were commonly used to predict maximum adsorption capacity, which helped to realize how optimized an adsorption system. The mutual correlation of adsorption capacity and equilibrium concentration was investigated by fitting experimental data using the Langmuir [24], Freundlich [21], Langmuir-Freundlich [37] and Dubinin-Radushkevich [40] isotherm models, respectively. The nonlinear forms of these models were given as:
\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e}
\]  \hspace{1cm} (6)

\[
q_e = K_F C_e^{1/n}
\]  \hspace{1cm} (7)

\[
q_e = \frac{q_m K_{F-L} C_e^n}{1 + K_{F-L} C_e^n}
\]  \hspace{1cm} (8)

\[
q_e = q_m \exp(-\beta \varepsilon^2) = q_m \exp(-\beta [RT \ln(1 + \frac{1}{C_e^m})]^2)
\]  \hspace{1cm} (9)

where \(q_e\) (mg g\(^{-1}\)) is the calculated adsorption capacity at equilibrium, \(C_e\) (mg L\(^{-1}\)) is the equilibrium nitrate concentration, \(K_L\) (L mg\(^{-1}\)) is the Langmuir constant, \(q_m\) (mg g\(^{-1}\)) is the fitting maximum adsorption capacity, \(K_F\) ((mg g\(^{-1}\)) (L mg\(^{-1}\))\(^{1/n}\)) is the Freundlich constant related to adsorption capacity, \(n\) is an empirical parameter related to adsorption intensity, \(K_{F-L}\) (L mg\(^{-1}\)) is the Langmuir-Freundlich adsorption constant, \(m\) is the heterogeneity factor, \(\beta\) (mol\(^2\) kJ\(^{-2}\)) is a constant related to the adsorption energy, \(\varepsilon\) (kJ mol\(^{-1}\)) is Polanyi potential, \(R\) (8.314 J mol\(^{-1}\) K\(^{-1}\)) is the universal gas constant, \(T\) (K) is the temperature in Kelvin. In Dubinin-Radushkevich isotherm model, the unit of the equilibrium nitrate concentration \((C_e)\) should be mol L\(^{-1}\).

In addition to correlation coefficient \((R^2)\), chi-square analysis \((\chi^2)\) and normalized standard deviation \((NSD)\) were employed to reasonably evaluate the validity of various models, which were defined as \([41,42]\):

\[
\chi^2 = \sum\frac{(q_e^{exp} - q_e^{calc})^2}{q_e^{calc}}
\]  \hspace{1cm} (10)

\[
NSD(\%) = 100 \times \sqrt{\frac{\sum[(q_e^{exp} - q_e^{calc})/q_e^{exp}]^2}{N - 1}}
\]  \hspace{1cm} (11)

where \(q_e^{exp}\) (mg g\(^{-1}\)) is the experimental equilibrium adsorption capacity, \(q_e^{calc}\) (mg g\(^{-1}\)) is the adsorption capacity calculated from models, \(N\) is the number of measurements.
Fig. 6. Adsorption isotherm for nitrate adsorption on granular chitosan-Fe\textsuperscript{3+} complex: Langmuir isotherm (the dash-dotted line), Freundlich isotherm (the dash line), Langmuir-Freundlich isotherm (the solid line) (a); Dubinin-Radushkevich isotherm (b).

Table 1

The corresponding information was shown in Fig. 6 and Table 1. The essential feature of Langmuir isotherm could be conveyed by a dimensionless constant separation factor ($R_L$), which was defined as [37]:

$$R_L = \frac{1}{1 + K_L C_0}$$  \hspace{1cm} (12)

It was generally stated that the $R_L$ value with the range $0 < R_L < 1$ indicated favorable, while the $n$ value in the range from 2 to 10 represented good [43]. It was obvious that the calculated $R_L$ and $n$ values in this study were 0.21 and 2.77 respectively, suggesting nitrate adsorption on the granular chitosan-Fe\textsuperscript{3+} complex was favorable. It was difficult to decide which isotherm was better fitted with the experimental data because the $R^2$ values exceeded 0.97 for the first three isotherm models. The $\chi^2$ and NSD values of Freundlich and Langmuir-Freundlich isotherm outdistanced those of Langmuir isotherm. Additionally, the $m$ value of Langmuir-Freundlich isotherm was not more than 1. These results indicated nitrate adsorption on granular chitosan-Fe\textsuperscript{3+} complex was a multilayer adsorption.

The relatively high correlation coefficient ($R^2 = 0.998$) reflected that the experimental data was also well described by the D-R isotherm, and that the fitting $\beta$
value could logically predict the mean free energy $E$ (kJ mol$^{-1}$) that could be calculated as [2]:

$$E = \frac{1}{\sqrt{2\beta}}$$  (13)

It was known that adsorption type was physical adsorption ($E < 8$ kJ mol$^{-1}$) or ion exchange ($8$ kJ mol$^{-1} < E < 16$ kJ mol$^{-1}$). The $E$ value obtained in this study was found to be 10.46 kJ mol$^{-1}$, revealing nitrate adsorption on granular chitosan-Fe$^{3+}$ complex was ion exchange, which was in agreement with other study where cetylpyridinium bromide (CPB) modified zeolite adsorbed nitrate [2].

3.6 Adsorption kinetics

In order to accurately reflect the variation trend of nitrate concentration with time and reveal the reaction pathway of adsorption process, several kinetic models were employed to examine the experimental data. The nonlinear pseudo-first-order and pseudo-second-order kinetic models were expressed as follows [44]:

$$q_t = q_e[1 - \exp(-k_1 t)]$$  (14)

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$$  (15)

where $q_e$ (mg g$^{-1}$) and $q_t$ (mg g$^{-1}$) represent the amount of nitrate adsorbed at equilibrium and at time $t$, respectively, $k_1$ (min$^{-1}$) and $k_2$ (g mg$^{-1}$ min$^{-1}$) denote the pseudo-first-order and pseudo-second-order rate constants, separately, $t$ (min) is the contact time.

In addition, the intraparticle diffusion model [45] was utilized to predict whether intraparticle diffusion was rate-determining step, which was given as:

$$q_t = k_p t^{0.5} + C$$  (16)

where $k_p$ (mg g$^{-1}$ min$^{-0.5}$) is the intraparticle diffusion rate constant, $C$ (mg g$^{-1}$) is the intercept related to the thickness of the boundary layer.
Table 2
Kinetic constants for adsorption of nitrate on the chitosan-Fe\textsuperscript{3+} complex.

It was observed from Fig. 7a that adsorption reaction was rapid in the first 15 min, followed by a sluggish stage until equilibrium. The equilibrium time of granular chitosan-Fe\textsuperscript{3+} complex (1.5 h) was inferior to that of chitosan hydrogel beads (10 h) [37] and organoclay (4 h) [1]. Compared with the pseudo-first-order kinetic, it was evident from Table 2 that the pseudo-second-order kinetic was fitted well with the experimental data in terms of correlation coefficient. For the intraparticle diffusion model (Fig. 7b), three segments of straight line could perfectly match a fitting curve of $q_t$ versus $t^{0.5}$, implying intraparticle diffusion was not an exclusive rate-determining step. Nitrate adsorption involved three steps [44]: a rapid external surface diffusion process (step 1), a slow intraparticle diffusion stage (step 2) and a dynamic adsorption-desorption equilibrium (step 3). These three processes often occurred simultaneously.

3.7 Thermodynamic parameters

Temperature was practically regarded as a key factor adjusting reaction rate and affecting adsorption capacity. The results with respect to the effect of temperature on nitrate removal were shown in Table 3. It was evident that the adsorption capacity slightly declined with the rise of temperature. The increase in desorption trend of
nitrate ions from adsorption sites to bulk solution might be applied to account for this phenomenon.

The results as mentioned above were further verified by thermodynamic parameters, such as Gibbs free energy change ($\Delta G^o$), enthalpy change ($\Delta H^o$) and entropy change ($\Delta S^o$). The $\Delta G^o$ (kJ mol$^{-1}$) value was calculated using the following equation [32]:

$$\Delta G^o = -RT \ln K_d$$

(17)

where $R$ (8.314 J mol$^{-1}$ K$^{-1}$) is the universal gas constant, $T$ (K) is the temperature in Kelvin, $K_d$ (mL g$^{-1}$) is the distribution coefficient reflecting the selectivity for nitrate ions. The $K_d$ value was calculated as follows [43]:

$$K_d = \frac{q_e}{C_e}$$

(18)

where $q_e$ (mg g$^{-1}$) and $C_e$ (mg mL$^{-1}$) is the adsorption capacity on granular chitosan-Fe$^{3+}$ complex and equilibrium concentration in bulk solution, respectively. The $\Delta S^o$ (J mol$^{-1}$ K$^{-1}$) and $\Delta H^o$ (kJ mol$^{-1}$) values could be estimated from the intercept and slope of linear plot of $\ln K_d$ versus $1/T$, respectively through the following equation [44]:

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$

(19)

Fig. 8. The plot of $\ln K_d$ versus $1/T$ for nitrate adsorption on granular chitosan-Fe$^{3+}$ complex.

Table 3
Thermodynamic parameters for nitrate adsorption on the chitosan-Fe$^{3+}$ complex.

Fig. 8 showed the exothermic nature of nitrate adsorption was confirmed by the negative $\Delta H^o$ value. The negative value of $\Delta G^o$ at various temperatures indicated that
adsorption reaction was a thermodynamically feasible and spontaneous process. These results were in agreement with other studies where crosslinked chitosan-Fe(III) complex adsorbed textile dye [21] and Cr(IV) [22]. The higher negative of $\Delta G^\circ$ with the increase in temperature revealed nitrate adsorption on granular chitosan-Fe$^{3+}$ complex was more likely to occur at higher temperature. The positive value of $\Delta S^\circ$ clearly showed the affinity of granular chitosan-Fe$^{3+}$ complex for nitrate ions and the increase in the randomness at the solid/solution interface during nitrate adsorption.

3.8 Regeneration

High adsorption capacity and good reusability were of utmost importance for any adsorbent, which would significantly promote economic value of adsorption method. In the present study, desorption efficiencies of 0.1 M NaCl, 0.1 M NaOH and 0.1 M Na$_2$SO$_4$ solution were found to be 84.3%, 95.3% and 93.8%, respectively. Consequently, granular chitosan-Fe$^{3+}$ complex was better than layered double hydroxide whose desorption efficiency was less than 2% [46]. It was evident that these desorption reagents could efficiently regenerate granular chitosan-Fe$^{3+}$ complex based on ion exchange reaction, which conduced to recovering nitrate from nitrate-contaminated water. However, when regenerated granular chitosan-Fe$^{3+}$ complex was firstly applied to adsorb nitrate, nitrate removal efficiencies were 78.1%, 0.8% and 22.5% for NaCl, NaOH and Na$_2$SO$_4$ solution, respectively. These results were explained by the fact that hydroxide and sulphate ions irreversibly occupied adsorption sites during regeneration, and thereby available adsorption sites for the first reuse significantly decreased. Moreover, nitrate removal efficiency slightly decreased from 78.1% to 76% undergoing four circles using 0.1 M NaCl solution as the eluent, indicating there were few irreversible adsorption sites on adsorbent surface [13]. Therefore, NaCl was a promising desorption reagent.
4 Conclusion

Granular chitosan-Fe$^{3+}$ complex had high performance for nitrate adsorption. The maximum adsorption capacity was 8.35 mg NO$_3^-$ N g$^{-1}$ based on Langmuir-Freundlich model. Granular chitosan-Fe$^{3+}$ complex had relatively large particle size (1.04-1.16 mm) and short equilibrium time (1.5 h). XRD analysis indicated that granular chitosan-Fe$^{3+}$ complex was an amorphous material. The BET specific surface area, total pore volume and average pore size were 8.98 m$^2$ g$^{-1}$, 0.019 cm$^3$ g$^{-1}$ and 56.94 Å, respectively. The point of zero charge was obtained at pH 5.4. Adsorption process infrequently suffered from initial pH and temperature, reflecting high chemical stability and good environmental adaptation. The adverse influence of sulphate ions on nitrate adsorption was mostly significant compared with other anions (Cl$^-$, HCO$_3^-$, F$^-$), while commonly cations (K$^+$, Na$^+$, NH$_4^+$, Ca$^{2+}$, Mg$^{2+}$) rarely interfered with nitrate adsorption. Nitrate adsorption was mainly attributed to ion exchange and electrostatic attraction. Thermodynamic study revealed that nitrate adsorption on granular chitosan-Fe$^{3+}$ complex was a spontaneous and exothermic process. Granular chitosan-Fe$^{3+}$ complex could be easily regenerated using NaCl solution.

Acknowledgements

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References


Table 1

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$K_F$ = (mg g$^{-1}$) (L mg$^{-1}$)$^{1/n}$
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Fig. 1

(a) (b) 

c) (d) 

(d) 

Pore diameter range (nm) 

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Fig. 2
Fig. 3
Fig. 4
Fig. 5

![Bar chart showing nitrate removal efficiency for different co-existing ions. The x-axis represents various ions (Blank, K⁺, Na⁺, NH₄⁺, Ca²⁺, Mg²⁺, CI⁻, HCO₃⁻, F⁻, SO₄²⁻) and the y-axis represents nitrate removal efficiency (%). The bar heights indicate the efficiency for each ion, with Blank showing the highest efficiency.]
Fig. 6

(a) Plot showing the experimental data and the Langmuir, Freundlich, and Langmuir-Freundlich models. The x-axis represents the concentration ($C_e$) in mg L$^{-1}$, and the y-axis represents the adsorption capacity ($q_e$) in mg g$^{-1}$. The symbols and lines indicate the different models.

(b) Plot depicting the adsorption capacity ($q_e$) in mol g$^{-1}$ as a function of the concentration ($C_e$) in mol L$^{-1}$. The symbols represent the experimental data, and the lines show the Dubinin-Radushkevich model.
Fig. 8

![Graph showing lnK vs 1/T x 10^3 (1/K)]